Kinetics of physical adsorption of ethane on Ir(110)-(1×2): Molecular beam reflectivity measurements and Monte Carlo simulations

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Experimental results, obtained using a reflectivity method, for the probability of physical adsorption of ethane on the Ir(110)-(1×2) surface are presented. We analyze these results using Monte Carlo simulations and show that physical adsorption can occur either directly or through a precursor state in which an ethane molecule is trapped in a second layer above a first layer of physically adsorbed ethane. From the Monte Carlo simulations, we are able to establish that the energy barrier for desorption of an ethane molecule from the precursor state is ~4.5 kcal/mol. We also find that the energy barrier for diffusion of an ethane molecule on top of a monolayer of physically adsorbed ethane on the Ir(110) surface is ~3.7 kcal/mol.

I. INTRODUCTION

The kinetics of precursor-mediated surface processes have been widely studied.[1] The role of the precursor state in the process of adsorption, in particular, has been intensively investigated using macroscopic approaches which treat the microscopic configuration of the adsorbed layer in a statistical manner.[2-13] There has also been an investigation in which Monte Carlo simulations were used to study the effect on precursor-mediated adsorption of the microscopic configuration of the adsorbed layer around each adsorption site.[14] These studies have pointed to the importance of the precursor state in influencing the kinetics of adsorption. In this paper, we present a precursor-mediated model for the molecular adsorption of ethane on the Ir(110)-(1×2) surface. We compare the results of Monte Carlo simulations of this model with molecular beam reflectivity measurements of the probability of molecular adsorption. The energy of the molecular beam was varied between ~2.2 and 10.0 kcal/mol by a combination of seeding and variation of the nozzle temperature. The surface temperature in the experiment was maintained constant at ~77 K. The partial pressure P_E of ethane at time t in the scattering chamber is used as a measure of the flux of ethane molecules that do not adsorb. Hence, the probability of adsorption at time t is $(P_S - P_E)/P_S$, where P_S is the partial pressure of ethane in the chamber due to scattering from a saturated surface. Both P_E and P_S are corrected for a small effusive component of the flux. Complete details of the experimental procedure will be published elsewhere.[15]

II. MODEL AND SIMULATION

The process of molecular adsorption of ethane on Ir(110)-(1×2) is modeled as follows. Molecular adsorption occurs either directly when an ethane molecule impinges upon the bare iridium surface, or indirectly when an ethane molecule impinges upon a previously adsorbed ethane molecule. The "extrinsic"[16] precursor in the latter case is a mobile ethane molecule trapped on top of a layer of molecularly adsorbed ethane. When an ethane molecule impinges upon the bare iridium surface, the probability that it accommodates thermally and becomes molecularly adsorbed is p_0. This is the zero coverage limit of the experimentally measured probability of adsorption. On the other hand, when an ethane molecule impinges upon a previously adsorbed ethane molecule, the probability that it accommodates thermally and becomes trapped as an "extrinsic" precursor is p_1. Clearly, p_1 is larger than p_0 because of a better match of masses and the existence of a softer potential, both of which facilitate better momentum transfer in the case of a collision with an adsorbed ethane molecule compared to the case of a collision with the bare iridium surface. When an ethane molecule becomes trapped above a layer of molecularly adsorbed ethane, it can either migrate on top of this layer until it reaches a vacant site on the iridium surface or it can desorb from the surface. We model the iridium surface by a square lattice of adsorption sites, and the migration of a trapped molecule of ethane by nearest-neighbor hops on top of the molecularly adsorbed ethane.

The Monte Carlo simulations are performed as follows. Each site on a square lattice of size (400×400) is allowed to be in one of three possible states: the site can be vacant; the site can be occupied by a molecularly adsorbed particle; or the site can be occupied by a molecularly adsorbed particle and a particle trapped in the precursor state. A site on the lattice is selected at random. If it is occupied by a trapped particle, then the particle is allowed either to hop to a nearest-neighbor site or to desorb. The choice is determined as follows. The trapped particle has a probability of 1/5 of attempting to move in each of five directions: the four lattice directions in the plane of the surface and the direction into the gas phase. If one of the lattice directions is chosen, the particle successfully moves to the nearest-neighbor site in that direction with a probability of p_m. If the direction into the gas phase is chosen, the particle successfully desorbs with a probability of p_d. If the site chosen is vacant, or is occupied by only a molecularly adsorbed particle, then a particle from the gas phase impinges upon it with a probabil-

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ity of p_f. If the site chosen is vacant, then the impinging particle adsorbs molecularly with a probability of p_0. If the site chosen is occupied by a molecularly adsorbed particle, then the impinging particle is trapped with a probability of p_1. Upon completion of this procedure, the time is increased by one Monte Carlo step, another site is selected at random, and the procedure is repeated. The quantity measured in the reflectivity experiments is the partial pressure of ethane as a function of time. From the Monte Carlo simulations, we obtain the values of n_i the number of particles impinging upon the lattice, and n_r the number of particles "reflecting" from the lattice in each Monte Carlo step/site. The quantity n_r includes both the particles that impinge upon and fail to be adsorbed molecularly or trapped, and the previously trapped particles that desorb from the lattice. The quantity that is obtained from the reflectivity experiments is, therefore, $(n_i - n_r)/n_i$. It should be noted that this is equal to the quantity n_a/n_i, where n_a is the number of particles molecularly adsorbing per Monte Carlo step/site, only when the rate of accumulation of the number of trapped ethane molecules in the second layer at any instant of time is vanishingly small.

The values of p_0 used in the simulations are obtained from the zero coverage limit of the experimentally measured probability of adsorption. The values of p_1 used for each beam energy are shown in Table I, the best fit values ranging from unity at a beam energy of 2.2 kcal/mol to 0.95 at a beam energy of 10.0 kcal/mol. In principle, both p_0 and p_1 are functions of the beam energy although, as seen in Table I, the dependence of p_1 on the beam energy is only a weak one. On the other hand, in our model p_m and p_d must not be dependent on the beam energy, because the trapped particle is assumed to be completely accommodated thermally to the surface. In the experiments the surface temperature is kept constant at ~77 K. Hence, for the simulations to be consistent physically, it is necessary that the same values of p_m and p_d successfully describe the experimental results at all beam energies. We choose p_m to be unity, and vary the ratio of p_d/p_m. As a result, we have set the time scale of the simulation to be the time scale for a trapped ethane molecule to hop from one site to the next. The parameter p_f is the probability, in each Monte Carlo step, that a gas phase molecule impinges upon each site. This parameter can, in principle, be determined from an accurate measurement of the flux of ethane in the molecular beam used in the experiments. If each Monte Carlo step corresponds to a real time of τ_r, then the incident flux would be p_f/τ_r site^{-1}s^{-1}. A crude estimate of this flux in the experimental measurements is 0.1 σ^{-1}s^{-1}, where σ is the area occupied by one adsorbed ethane molecule when the surface is saturated with one monolayer of ethane at 77 K. This is because the experiments take ~10 s, and, as shown below, the final fractional coverages are only slightly greater than one monolayer. In the simulations, however, we used a range of values of p_f, and chose the resulting value of the flux that best fits the experimental results. As may be seen in Table I, these values are gratifyingly close to 0.1 σ^{-1}s^{-1}.

As noted above, the quantity obtained from the reflectivity measurements $(P_E - P_S)/P_S$ corresponds to $(n_i - n_r)/n_i$, and is only equal to n_a/n_i when there is no accumulation of a second layer of trapped ethane molecules. In the simulations this is the case when the parameter p_f is vanishingly small compared to p_d and p_m. The procedure for performing the Monte Carlo simulations in this case is as follows. First, we determine the probability of molecular adsorption for a fixed coverage on the surface, and then we increase the coverage on the surface. The probability of molecular adsorption is determined by introducing test particles one at a time, and counting the fraction that adsorbs molecularly. If a test particle impinges on a vacant site, then molecular adsorption occurs with a probability of p_0. If the test particle impinges on a site which is already occupied by a molecularly adsorbed particle, then it traps with a probability of p_1. A trapped particle is allowed to attempt to move in one of the four lattice directions or in the direction into the gas phase. Each of these directions is picked with a probability of 1/5. An attempted hop to a nearest-neighbor site is successful with a probability of p_m. If the test particle attempts to move into the gas phase, it desorbs with a probability of p_d. A test particle is allowed to migrate on the lattice by nearest-neighbor hops until it either desorbs or reaches a vacant lattice site, whereupon it immediately adsorbs molecularly. Then the next test particle is introduced. In order to obtain the probability of molecular adsorption at a constant coverage, the configuration on the lattice is not updated even if a test particle molecularly adsorbs. For each datum point we introduce 2000 test particles. The configuration on the lattice is updated as follows. A certain number of test particles are introduced, again one at a time. However, now the positions of the test particles which adsorb molecularly are recorded. A test particle which adsorbs molecularly into a site at which an earlier test particle had adsorbed is not counted. After N particles have been introduced, the configuration is updated by using the recorded positions of the molecularly adsorbed test particles. Time is increased by N/FL^2, where F is the flux from the gas phase in units of site^{-1}s^{-1} and L^2 is the number of sites on the lattice. For our

TABLE I. Values of parameters used in the simulations and experiments. The energy of the beam E_i is in units of kcal/mol and the incident angle θ_i is in degrees. The energy barrier for desorption E_d is in units of kcal/mol and the fluxes are in units of $s^{-1}\sigma^{-1}$ for each beam energy, where σ is the area occupied by a molecularly adsorbed ethane molecule in a saturated first layer on the Ir (110)-(1×2) surface at 77 K. The probability of adsorption on the clean surface (in the limit of zero coverage) is p_0, and the probability of trapping on top of an adsorbed ethane molecule is p_1. The value of p_d/p_m, where p_d is the probability of success of an attempted desorption event and p_m is the probability of success of an attempted hop by a trapped particle, is 0.005 for all the simulation results reported here.

Set	E_i	θ_i	p_0	p_1	E_d	Flux
a	2.2	0	0.95	1.00	4.55	0.087
b	3.7	45	0.90	1.00	4.57	0.077
c	5.2	45	0.83	0.97	4.53	0.102
d	6.6	0	0.68	0.96	4.52	0.107
e	10.0	45	0.50	0.95	4.53	0.104
f	10.0	22.5	0.45	0.95	4.55	0.085

simulations we used $N = 1600$, so that we obtain the adsorption probabilities for every fractional surface coverage increment of 0.01. This procedure is then repeated with the new configuration. It should be noted that the time increment is not dependent upon the actual number of migration steps that are taken by the test particles, since the time for each migration step is infinitesimally small compared to that between subsequent particle impingements on the surface when $p_f = 0$. Note that in simulations in which p_f is vanishingly small both desorption and migration occur infinitely fast on the time scale of the particle flux onto the surface. Hence, it is not possible to establish, via comparison with experimental results, the absolute rates of desorption and migration. This, however, can be done with simulations in which p_f is not zero.

III. RESULTS AND DISCUSSION

The results for a beam energy of 6.6 kcal/mol are shown in Figs. 1 and 2.[17] In both figures, the crosses are the experimental data obtained from the reflectivity measurements. The ordinate has been labeled as the probability of adsorption although for the experimental data it is really $(P_S - P_E)/P_S$, which corresponds to the quantity $(n_i - n_r)/n_i$ obtained from the simulations. The abscissa is time in units of 0.1 s. For this beam energy, the experiment was performed at a normal angle of incidence. For other values of the incident angle, the time has to be scaled by $\cos\theta_i$, where θ_i is the angle of incidence, to account for the dependence of the incident flux upon the incident angle at a constant beam intensity. The results of simulations in which $p_f = 0$ and $p_0 = 0.68$ are plotted as the line in Fig. 1. The values of the other parameters for these simulations are $p_1 = 0.96$ and $p_d/p_m = 0.005$. As mentioned earlier, p_0 is equal to the zero coverage limit of the experimentally measured probability of adsorption, which is ~ 0.68 in this case. It can be seen in Fig. 1 that the experimental results have a

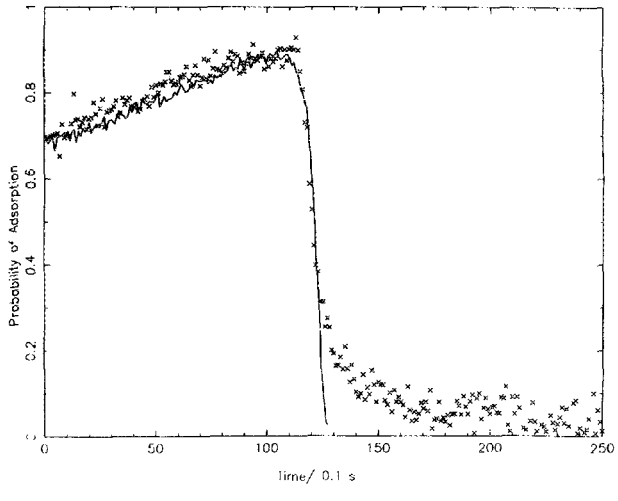

FIG. 1. Experimental data for a beam energy of ~ 6.6 kcal/mol ($\times$) and results from simulations in the zero flux limit (—) the values of the parameters used in the simulations are $p_0 = 0.68$, $p_1 = 0.96$, and $p_d/p_m = 0.005$. The abscissa is time in units of 0.1 s. The parameters for the simulations displayed here can be found in row d of Table I.

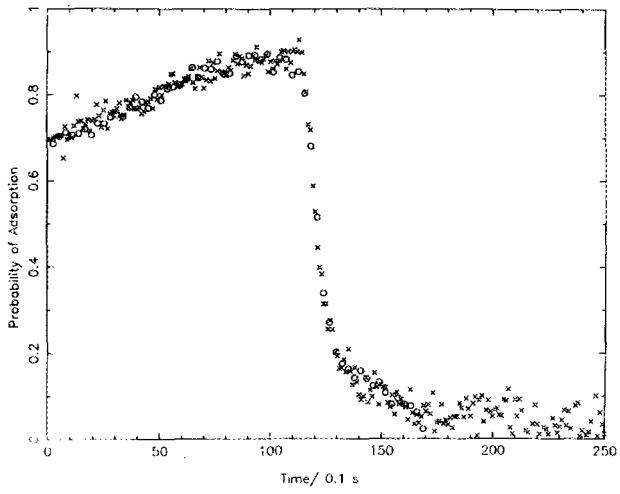

FIG. 2. Experimental data for a beam energy of ~ 6.6 kcal/mol ($\times$), as in Fig. 1. Results from simulations in which the value of p_f is 6×10^{-5} (O), and thus the flux which is equal to p_f/τ_r is not zero. The abscissa for the Monte Carlo data has been converted from Monte Carlo steps/site to real time. The conversion factor τ_r gives the number of seconds in real time to which each Monte Carlo step/site corresponds. This, as explained in the text, enables an absolute determination of the desorption rate from the second layer. The units of the abscissa are 0.1 s.

longer "tail" than the results from simulations in which $p_f = 0$. Except for this tail the simulations agree rather well with the experimental data. The simulations are sufficiently sensitive that significant deviations from this agreement are observed if p_d/p_m is < 0.001 or > 0.01. From the presence of the tail in the experimental data and its absence from the simulation results when $p_f = 0$, it can be inferred that at 77 K a second layer of ethane begins to accumulate on the surface when the first layer is nearly saturated. It is possible that this kind of tail could result from an equilibrium between the first monolayer of ethane and the gas phase rather than the second layer and the gas phase. However, the desorption barrier for a molecularly adsorbed ethane molecule from the Ir(110)-(1×2) surface is ~ 7.5 kcal/mol.[18] As will be seen below, this tail indicates equilibration between the gas phase and a layer of adsorbed ethane with a desorption barrier of 4.5 kcal/mol. Hence, the tail in the experimental data is much too long to be accounted for by desorption from the first monolayer.

It can be seen in Fig. 2 that by simply allowing p_f to be nonzero, the simulations can produce the tail observed in the reflectivity experiments. In the simulations in which p_f is not zero, the time is measured in Monte Carlo steps/site. By fitting the results of these simulations to the experimental data, it is possible to determine the real time τ_r that corresponds to each Monte Carlo step/site. The best fit is obtained by the following procedure. The values of p_1 and p_d/p_m that best fit the experimental data, except for the tail, are determined using simulations in which p_f is set equal to zero. Then using these values of p_1 and p_d/p_m, simulations with various nonzero values of p_f are performed, and the best fit value of p_f can be obtained. Note that in many Monte Carlo simulations it is convenient to use ν^{-1}, the reciprocal of the frequency of the frustrated translational degree of free-

dom parallel to the surface, as the time scale so that each Monte Carlo step corresponds to an attempted hop. Since we have set p_m to be unity, the time-scale in these simulations is the time scale at which successful hops occur. Hence, τ_r can be much larger than ν^{-1}, the latter of which typically has a value of $\sim 10^{-13}$ s.

The rate of desorption of a trapped particle is $p_d/5$ per Monte Carlo step. The factor of 1/5 arises from allowing a trapped particle to attempt to move with equal probability in each of five directions, as discussed above; and desorption is allowed in only one of these directions. Hence, the rate of desorption from the second layer of ethane is given by $R_d = p_d/5\tau_r$. Similarly, the flux incident upon the surface is given by p_f/τ_r. Therefore, we can calculate the desorption energy E_d and the incident flux by comparing the results of the simulations to the experimental data and obtaining the best fit value of p_f, as described above. These quantities are summarized in Table I for each beam energy. The results plotted in Fig. 2 as O are from simulations in which $p_f = 6\times 10^{-5}$. We find that deviations between the experimental tail and the Monte Carlo tail begin to be apparent if p_f is $\gtrsim 1\times 10^{-4}$ or if p_f is $\lesssim 1\times 10^{-5}$. The calculated values of the incident flux indicate that the fluxes used in the reflectivity measurements vary by $\sim 20\%$, which is physically reasonable. The uncertainty in the calculated value of the flux arises from the uncertainty in the value of τ_r. This same uncertainty implies an uncertainty of ~ 0.05 kcal/mol in the value of E_d. However, there is a much greater uncertainty due to a lack of information concerning the value of the preexponential factor.[19] For the simulation results shown in both Figs. 1 and 2, the value of p_d/p_m is 0.005. This is the ratio of the probability of successful desorption to the probability of successful migration. Hence, the difference between the respective energy barriers $\delta E \equiv E_d - E_m$ is ~ 800 cal/mol, assuming that the preexponential factors for these two processes are equal. This implies that E_m is $\simeq 3.7$ kcal/mol. If the preexponential factor for desorption is larger than that for migration, as might be expected, then δE would be somewhat larger than 800 cal/mol and E_m would be < 3.7 kcal/mol.[20] Simulations were also performed for $p_d/p_m = 0.01$ and $p_d/p_m = 0.001$ to estimate the sensitivity of the fit. These runs allow us to conclude that the uncertainty in δE for a fixed ratio of the preexponential factors is ~ 200 cal/mol.

IV. CONCLUSIONS

The probability of molecular adsorption of ethane on Ir(110)-(1×2) has been measured by molecular beam reflectivity experiments and has been analyzed using Monte Carlo simulations. The experimental results show that the probability of adsorption initially increases as the fractional coverage of ethane increases from zero and goes through a maximum at higher surface coverage. This behavior is well described by a model which allows both direct molecular adsorption and precursor-mediated molecular adsorption. The precursor state here is one in which a gas phase ethane molecule impinges upon a previously adsorbed ethane molecule and is trapped as an "extrinsic" precursor. Our model assumes complete thermal accommodation of such a trapped ethane molecule which can, subsequently, either migrate to the bare iridium surface and become molecularly adsorbed or desorb from the surface. The Monte Carlo simulations of the model were performed on a square lattice even though the Ir(110)-(1×2) surface has a rectangular unit cell. This "anisotropy" of the iridium surface need not be considered, however, because migration of the trapped ethane molecules occurs on top of a layer of molecularly adsorbed ethane which presents an "isotropic" surface to a trapped ethane molecule. This procedure is also justified by the excellent agreement between the simulation results and the experimental data.

The Monte Carlo simulations provide a good understanding of the process of adsorption for this system. In particular, the tail which is observed in the experiment is shown to be the result of a small accumulation ($\sim 5\%$ of a full layer) of trapped ethane in a second adsorbed layer when the first monolayer approaches saturation coverage. Using only one set of values of p_d/p_m and p_f/p_m, it is possible to fit the experimental results for all the beam energies that were used. From the fit between the experimental data and the Monte Carlo simulations, it is possible to determine that the energy barrier for desorption of ethane from the second layer is $\sim 4.5 \pm 0.3$ kcal/mol, and the energy barrier for migration of trapped ethane on top of the first layer is $\sim 3.7 \pm 0.2$ kcal/mol.

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[20] For example, if the ratio of the preexponential factors $k_d^{(0)}/k_m^{(0)} = 100$, then $\delta E = 1.5$ kcal/mol, and E_m would be 3.0 ± 0.2 kcal/mol.